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**UNITED STATES PATENT APPLICATION**

of

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for

**BIODEGRADABLE POLYMER BLENDS FOR USE IN MAKING  
FILMS, SHEETS AND OTHER ARTICLES OF MANUFACTURE**

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## BACKGROUND OF THE INVENTION

### 1. The Field of the Invention.

The present invention relates generally to biodegradable polymer blends and articles manufactured therefrom. More particularly, the present invention relates to blends of two or more biopolymers and/or blends of biopolymers and fillers that yield sheets and films having improved physical properties, such as flexibility, elongation and/or dead-fold. The biodegradable polymer blends may be suitable for a number of applications, such as in the manufacture of disposable wraps, bags and other packaging materials or as coating materials.

### 2. The Relevant Technology.

As affluence grows, so does the ability to purchase and accumulate more things. Never before in the history of the world has there been such a large number of people with such tremendous buying power. The ability to purchase relatively inexpensive goods, such as books, tools, toys and food, is a luxury enjoyed by virtually all levels of society, even those considered to be at the poorer end of the spectrum. Because a large percentage of what is purchased must be prepackaged, there has been a tremendous increase in the amount of disposable packaging materials that are routinely discarded into the environment as solid waste. Thus, as society becomes more affluent, it generates more trash.

Some packaging materials are only intended for a single use, such as boxes, cartons, pouches, bags and wraps used to package items purchased from wholesale and retail outlets. Even the advent of computers and "paperless" transactions has not stemmed the rising tide of packaging wastes. Indeed, the onset of "e-commerce" has spawned a great mail-order fad, thus creating a whole new market of individually packaged and shipped items.

Moreover, the modern, fast-paced lifestyle has greatly disrupted traditional eating routines in which people prepared their own meals and sat down as a family or group. Instead, people grab food on the run, thus creating ever-increasing amounts of fast food

1 packaging materials that are used once and then discarded. In view of the high volume of  
2 disposable packaging materials being generated, some countries, particularly those in Europe,  
3 have begun to mandate either the recycling of fast food generated wastes or the use of  
4 packaging materials which are "biodegradable" or "compostable". Environmental activists  
5 commonly pressure companies that generate solid waste. As a result, large fast food chains  
6 such as McDonald's have been essentially forced to discontinue the use of certain  
7 nonbiodegradable packaging materials such as foamed polystyrene, either by government fiat  
8 or by pressure by environmental groups. McDonald's currently uses a combination of paper  
9 wraps and cardboard boxes as an interim solution until more environmentally friendly  
10 packaging materials can be made on a commercial basis. There is therefore an ever-present  
11 need to develop biodegradable alternatives to nonbiodegradable paper, plastics and metals.

12 In response to the demand for more environmentally friendly packaging materials,  
13 a number of new biopolymers have been developed that have been shown to biodegrade  
14 when discarded into the environment. Some of the larger players in the biodegradable  
15 plastics market include such well-known chemical companies as DuPont, BASF, Cargill-  
16 Dow Polymers, Union Carbide, Bayer, Monsanto, Mitsui and Eastman Chemical. Each of  
17 these companies has developed one or more classes or types of biopolymers. For example,  
18 both BASF and Eastman Chemical have developed biopolymers known as "aliphatic-  
19 aromatic" copolymers, sold under the trade names ECOFLEX and EASTAR BIO,  
20 respectively. Bayer has developed polyesteramides under the trade name BAK. Du Pont has  
21 developed BIOMAX, a modified polyethylene terephthalate (PET). Cargill-Dow has sold  
22 a variety of biopolymers based on polylactic acid (PLA). Monsanto developed a class of  
23 polymers known as polyhydroxyalkanoates (PHA), which include polyhydroxybutyrates  
24 (PHB), polyhydroxyvalerates (PHV), and polyhydroxybutyrate-hydroxyvalerate copolymers  
25 (PHBV). Union Carbide manufactures polycaprolactone (PCL) under the trade name TONE.

1 Each of the foregoing biopolymers has unique properties, benefits and weaknesses.  
2 For example, biopolymers such as BIOMAX, BAK, PHB and PLA tend to be strong but are  
3 also quite rigid or even brittle. This makes them poor candidates when flexible sheets or  
4 films are desired, such as for use in making wraps, bags and other packaging materials  
5 requiring good bend and folding capability. In the case of BIOMAX, DuPont does not  
6 presently provide specifications or conditions suitable for blowing films therefrom, thus  
7 indicating that it may not be presently believed that films can be blown from BIOMAX and  
8 similar polymers.

9 On the other hand, biopolymers such as PHBV, ECOFLEX and EASTAR BIO are  
10 many times more flexible compared to the more rigid biopolymers discussed immediately  
11 above. However, they have relatively low melting points such that they tend to be self  
12 adhering and unstable when newly processed and/or exposed to heat. While initially easily  
13 blown into films, such films are often difficult to process on a mass scale since they will tend  
14 to self adhere when rolled onto spools, which is typically required for sale and transport to  
15 other locations and companies. To prevent self-adhesion (or "blocking") of such films, it is  
16 typically necessary to incorporate a small amount (*e.g.* 0.15% by weight) of silica, talc or  
17 other fillers.

18 Another important criteria for sheets and films used in packaging is temperature  
19 stability. "Temperature stability" is the ability to maintain desired properties even when  
20 exposed to elevated or depressed temperatures, or a large range of temperatures, which may  
21 be encountered during shipping or storage. For example, many of the more flexible  
22 biopolymers tend to become soft and sticky if heated significantly above room temperature,  
23 thus compromising their ability to maintain their desired packaging properties. Other  
24 polymers can become rigid and brittle upon being cooled significantly below freezing (*i.e.*,  
25 0° C.). Thus, certain homopolymers or copolymers may not by themselves have sufficient  
26 stability within large temperature ranges.

1 In the case of the packaging of foods, such as refrigerated meats or fast foods, the  
2 packaging materials may be subjected to widely fluctuating temperatures, often being  
3 exposed to rapid changes in temperature. A biopolymer that may be perfectly suitable at  
4 room temperature, for example, may become completely unsuitable when used to wrap hot  
5 foods, particularly foods that emit significant quantities of hot water vapor or steam. In the  
6 case of meats, a wrapping that may be suitable when used at room temperature or below,  
7 such as at refrigeration or freezing temperatures, might become soft and sticky during  
8 microwave thawing of the meat. Of course, it would generally be unacceptable for a  
9 biopolymer to melt or adhere to the meat or fast food being served unless it was desired for  
10 some reason that the person actually consume the biopolymer.

11 Another factor that impacts whether a particular material is suitable for use as a wrap  
12 (e.g. sandwich or meat wrap) is whether sheets or films formed therefrom have suitable  
13 "dead-fold" properties. The term "dead-fold" is a measurement of the tendency of a sheet  
14 or film to remain in a desired orientation once used to encapsulate, enclose, wrap or  
15 otherwise enclose at least a portion of an item to be packaged. Wraps made from paper, for  
16 example, typically have modest to excellent dead fold properties depending on how the paper  
17 has been processed or treated. On the other hand, many plastic films or sheets (e.g.  
18 polyethylene) have very poor dead-fold properties such that they make very poor wraps.  
19 Instead, they are better suited for other uses, such as sacks, bags, pouches, coverings, etc.  
20 where good dead-fold is not necessary or desirable. In order to compensate for generally  
21 poor dead-fold properties, plastic wraps are typically manufactured to have high self-cling  
22 (e.g. SARAN WRAP). Self cling is a property having little to do with dead-fold, and is akin  
23 to the use of adhesives. One problem with self cling wraps is that they can be very difficult  
24 to handle. A self-cling wrap that is accidentally allowed to cling to itself before being used  
25 to wrap the substrate becomes useless and must be discarded and replaced with another  
26 length of self-cling wrap.

1 Paper also breathes (*i.e.* transmits gas) and has good water vapor transmission unless  
2 completely sealed with a wax or plastic. Plastic films and sheets, on the other hand,  
3 generally have very poor water vapor transmission and breathability. As a result, paper is  
4 a much better as a wrap for hot foods than plastic sheets because it permits the escape of  
5 water vapor. A plastic sheet, on the other hand, will retain virtually all of the water vapor,  
6 which condenses over time on the plastic surface and can make the food soggy, particularly  
7 a bun or slice of bread.

8 In view of the foregoing, it would be an advancement in the art to provide  
9 biodegradable polymers which could be readily formed into sheets and films that had  
10 strength and flexibility properties suitable for use as packaging materials and that had  
11 suitable temperature stability for a given use. In addition or alternatively, it would also be  
12 an advancement in the packaging art to provide improved biodegradable polymers that could  
13 be formed into sheets and films having sufficient dead-fold so that they could be folded,  
14 wrapped or otherwise manipulated in order to reliably enclose a substrate therein. In addition  
15 or alternatively, it would be a further advancement in the packaging art to provide improved  
16 biodegradable sheets and films that had enhanced breathability and water vapor transmission  
17 compared to conventional plastic sheets.

18 Such improved biopolymers, as well as sheets and films formed therefrom, are  
19 disclosed and claimed herein.  
20

One aspect of the invention involves blending at least one biopolymer having relatively high stiffness with at least one biopolymer having relatively high flexibility. For example, blends containing a relatively stiff BIOMAX polymer, a modified PET sold by Du Pont, with a relatively soft or flexible ECOFLEX, an aliphatic-aromatic copolymer sold by BASF, and/or EASTAR BIO, an aliphatic-aromatic copolymer sold by Eastman Chemical, have been shown to have strength and elongation properties which are superior to either biopolymer taken alone. Thus, the present invention provides blends that possess or demonstrate surprising synergistic effects.

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1 ECOFLEX actually exhibit higher elongation than ECOFLEX by itself, as well as higher  
2 break stress compared to either BIOMAX or ECOFLEX by themselves.

3 Other polymer blends have been developed, including but not limited to, a blend of  
4 ECOFLEX, PLA and thermoplastic starch (TPS) and a blend of BAK and TPS. In each case,  
5 blending a biopolymer having a relatively low glass transition temperature with a biopolymer  
6 having a relatively high glass transition temperature has resulted in polymer blends that, in  
7 many cases, exhibit the desired characteristics of each polymer by itself, in some cases  
8 exhibiting even better properties, while diminishing or minimizing the negative properties  
9 of each biopolymer by itself.

10 In general, biopolymers that may be characterized as being relatively "stiff" or less  
11 flexible include polymers which have a glass transition temperature greater than about  
12 10° C., while biopolymers that may be characterized as being relatively "soft" include  
13 polymers having a glass transition temperature less than about 0° C. "Stiff" biopolymers  
14 preferably have a glass transition temperature greater than about 15° C., more preferably  
15 greater than about 25° C., and most preferably greater than about 35° C. "Soft" biopolymers  
16 preferably have a glass transition temperature of less than about -4° C., more preferably less  
17 than about -10° C., more especially preferably less than about -20° C., and most preferably  
18 less than about -30° C.

19 In addition, "stiff" polymers are generally more crystalline, while "soft" polymers  
20 are generally less crystalline and more amorphous, particularly at room temperature.

21 The relatively stiff polymers, characterized as those polymers generally having a  
22 glass transition greater than about 10° C, will preferably have a concentration in a range from  
23 about 20% to about 99% by weight of the biodegradable polymer blend, more preferably in  
24 a range from about 55% to about 98% by weight, and most preferably in a range from about  
25 70% to about 95% by weight of the polymer blend (*i.e.*, the combined weight of the stiff and  
26 soft polymers).



1 The relatively soft polymers, characterized as those polymers generally having a  
2 glass transition less than about 0° C, will preferably have a concentration in a range from  
3 about 1% to about 80% by weight of the biodegradable polymer blend, more preferably in  
4 a range from about 2% to about 45% by weight, and most preferably in a range from about  
5 5% to about 30% by weight of the polymer blend.

6 Biopolymers within the scope of the present invention include, but are not limited  
7 to, synthetic polyesters, semi-synthetic polyesters made by fermentation (*e.g.*, PHB and  
8 PHBV), polyester amides, polycarbonates, and polyester urethanes. In another aspect, it is  
9 within the scope of the invention to optionally include a variety of natural polymers and their  
10 derivatives, such as polymers comprising or derived from starch, cellulose, other  
11 polysaccharides and proteins.

12 Although it is within the scope of the invention to include thermoplastic polymers  
13 based on starch that include a high boiling liquid plasticizer such as glycerine, propylene  
14 glycol and the like, it is preferable, when manufacturing wraps that are intended to come into  
15 contact with food products, to utilize thermoplastic starch polymers that are made without  
16 the use of such plasticizers, which can potentially diffuse into food. Preferred thermoplastic  
17 starch polymers for use in making food wraps may advantageously utilize the natural water  
18 content of native starch granules to initially break down the granular structure and melt the  
19 native starch. Thereafter, the melted starch can be blended with one or more synthetic  
20 biopolymers, and the mixture dried by venting, in order to yield a final polymer blend.  
21 Where it is desired to make food wraps or other sheets or films intended to contact food  
22 using a thermoplastic starch polymer made with a high boiling liquid plasticizer, it will be  
23 preferable to limit the quantity of such thermoplastic starch polymers to less than 10% by  
24 weight of the polymer mixture, exclusive of any solid fillers.

25 In another aspect, it is within the scope of the invention to include one or more  
26 nonbiodegradable polymers within the polymer blends. Such polymers may remain in

1 particulate form, or they may become thermoplastic during processing. In either case, the  
2 resulting polymer blends will tend to exhibit biodegradability so long as the  
3 nonbiodegradable polymers are included as a disperse, rather than a continuous, phase.

4 In another aspect, it is within the scope of the invention to incorporate inorganic and  
5 organic fillers in order to decrease self-adhesion, lower the cost, and increase the modulus  
6 of elasticity (Young's modulus) of the polymer blends. Examples of inorganic fillers include  
7 calcium carbonate, titanium dioxide, silica, talc, mica, and the like. Examples of organic  
8 fillers include wood flour, seeds, polymeric particles, ungelatinized starch granules, and the  
9 like. In addition, plasticizers may be used in order to impart desired softening and elongation  
10 properties.

11 In the case of sheets or films intended to be used as "wraps", such as wraps used to  
12 enclose meats, other perishable food items, and especially fast food items (*e.g.*, sandwiches,  
13 burgers and dessert items), it may be desirable to provide sheets and films having good  
14 "dead-fold" properties so that once folded, wrapped or otherwise manipulated into a desired  
15 orientation, such wraps will tend to substantially maintain their orientation so as to not  
16 spontaneously unfold or unwrap, as occurs with a large number of plastic sheets and films  
17 (*e.g.*, polyethylene). Dead-fold is a measure of the ability of a sheet or film to retain a crease,  
18 crinkle or other bend. It is measured independently of self cling, heat sealing, or the use of  
19 an adhesive to maintain a desired orientation.

20 In order to improve the dead-fold properties of sheets or films produced therefrom,  
21 biopolymer blends (optionally including fillers) may be engineered so as to yield films  
22 having a relatively high Young's modulus, preferably greater than about 100 MPa, more  
23 preferably greater than about 150 MPa, and most preferably greater than about 200 MPa. In  
24 general, increasing the concentration of the stiff biopolymer will tend to increase the Young's  
25 modulus and the resulting dead-fold properties. It should be understood, however, that

1 Young's modulus only loosely correlates to dead-fold and does not, in every case, serve to  
2 define or predict the dead-fold properties of a particular sheet or film.

3 Including an inorganic filler is another way to increase dead-fold. Thus, it has been  
4 found that adding significant quantities of an inorganic filler, such as greater than about 10%  
5 by weight of the overall mixture, preferably greater than about 15% by weight, more  
6 preferably greater than about 20% by weight, more especially preferably greater than about  
7 30% by weight, and most preferably greater than about 35% by weight of the overall mixture,  
8 greatly improves the dead-fold properties of sheets and films manufactured from polymers  
9 or polymer blends according to the invention.

10 Yet another way to increase the dead-fold properties is to increase the surface area,  
11 or "bulk hand feel" of a sheet, which is done by disrupting the generally smooth, planar  
12 nature of the sheet or film. This may be accomplished, for example, by embossing, crimping,  
13 quilting or otherwise texturing the sheet so as to have regularly spaced-apart or random hills  
14 and valleys rather than simply being a perfectly smooth, planar sheet. A sheet or film may  
15 be textured, for example, by passing the sheet or film through a pair of knurled or other  
16 embossing-type rollers. Such texturing increases the ability of a sheet to take and maintain  
17 a fold, thus improving the dead-fold properties of the sheet. Another way to increase the  
18 surface area of sheets and films according to the invention is to incorporate one or more  
19 particulate fillers that, at least a portion of which, have a particle size diameter equal to or  
20 greater than the thickness of the film or sheet.

21 When used to wrap foods, or whenever good dead-fold properties are desired, sheets  
22 and films according to the invention can be manufactured so as to have a dead-fold of at least  
23 about 50% (*i.e.*, when creased using a standard dead-fold test, the sheets and films will  
24 maintain at least about 50% of their original crease ). Preferably, such sheets and films will  
25 have a dead-fold greater than about 60%, more preferably greater than about 70%, and most  
26 preferably greater than about 80%. As will be shown hereafter, sheets and films according

1 to the invention have been developed that have a dead-fold approaching or equal to 100%  
2 (*i.e.*, when folded they remain folded absent the application of an external force sufficient  
3 to reverse the fold). By way of comparison, sheets and films made from polyethylene (*e.g.*,  
4 for use in making sandwich or garbage bags) typically have a dead-fold of 0%. Standard  
5 paper wraps commonly used in the fast food industry typically have a dead-fold between  
6 about 40-80%. Thus, sheets and films according to the invention have dead-fold properties  
7 that meet or exceed those of standard paper wraps, and which are many times greater than  
8 conventional plastic films and sheets, often orders of magnitude greater.

9 In some cases, it may be desirable for sheets and films according to the invention to  
10 have the feel and breathability of paper. As set forth above, particulate fillers, both organic  
11 and inorganic, can be used to increase the modulus of elasticity and dead-fold. Such fillers  
12 also advantageously create "cavitation" whenever the sheets or films are stretched during  
13 processing. Cavitation occurs as the thermoplastic polymer fraction is pulled in either a  
14 monoaxial or biaxial direction and the filler particles create a discontinuity in the film or  
15 sheet that increases in size during stretching. In essence, a portion of the stretched polymer  
16 pulls away from the filler particles, resulting in tiny cavities in the vicinity of the filler  
17 particles. This, in turn, results in greatly increased breathability and vapor transmission of  
18 the sheets and films. It also results in films or sheets having a touch and feel that much more  
19 closely resembles the touch and feel of paper, as contrasted with conventional thermoplastic  
20 sheets and films. The result is a sheet or wrap that can be used for applications that are  
21 presently performed or satisfied using paper products (*i.e.*, wraps, tissues, printed materials,  
22 etc.)

23 Articles of manufacture made according to the invention can have any desired  
24 thickness. Thicknesses of sheets and films may range from 0.0001" to 0.1" (about 2.5  
25 microns to about 2.5 mm). Sheets and films suitable for wrapping, enclosing or otherwise  
26 covering food items or other solid substrates will typically have a measured thickness

1 between about 0.0003" and about 0.01" (about 7.5-250 microns), and a calculated thickness  
2 between about 0.00015" and about 0.005" (about 4-125 microns). The measured thickness  
3 will typically be between 10-100% larger than the calculated thickness when the sheets and  
4 films are made from compositions that have a relatively high concentration of particulate  
5 filler particles, which can protrude from the surface of the sheet or film. This phenomenon  
6 is especially pronounced when significant quantities of filler particles having a particle size  
7 diameter that is larger than the thickness of the polymer matrix are used.

8 Another advantage of utilizing biopolymers in the manufacture of wraps is that  
9 biopolymers are generally able to accept and retain print much more easily than conventional  
10 plastics or waxed papers. Many plastics and waxes are highly hydrophobic and must be  
11 surface oxidized in order to provide a chemically receptive surface to which ink can adhere.  
12 Biopolymers, on the other hand, typically include an abundant fraction of oxygen-containing  
13 moieties, such as ester, amide and/or urethane groups, to which inks can readily adhere.

14 The sheets and films according to the invention may comprise a single layer or  
15 multiple layers as desired. They may be formed by mono- and co-extrusion, casting and film  
16 blowing techniques known in the art. Because they are thermoplastic, the sheets can be post-  
17 treated by heat sealing to join two ends together to form sacks, pockets, pouches, and the  
18 like. They can be laminated onto existing sheets or substrates. They can also be coated  
19 themselves.

20 These and other features of the present invention will become more fully apparent  
21 from the following description and appended claims, or may be learned by the practice of the  
22 invention as set forth hereinafter.  
23

## BRIEF DESCRIPTION OF THE DRAWINGS

In order that the manner in which the above-recited and other advantages and objects of the invention are obtained, a more particular description of the invention briefly described above will be rendered by reference to a specific embodiment thereof which is illustrated in the appended drawings. Understanding that these drawings depict only a typical embodiment of the invention and are not therefore to be considered to be limiting of its scope, the invention will be described and explained with additional specificity and detail through the use of the accompanying drawings, in which:

Figure 1 is a plot of the percent elongation at break versus the applied strain rate for various neat and blended polymer films;

Figure 2 is a plot of the percent elongation of various neat polymer and blended polymer films versus the concentration of ECOFLEX within the films at a fixed strain rate of 500 mm/min.;

Figure 3 is a plot of the percent elongation of various neat polymer and blended polymer films versus the concentration of ECOFLEX within the films at a fixed strain rate of 1000 mm/min.;

Figure 4 is a plot of the break stress versus the applied strain rate for various neat and blended polymer films;

Figure 5 is a plot of the break stress of various neat polymer and blended polymer films versus the concentration of ECOFLEX within the films at a fixed strain rate of 500 mm/min.;

Figure 6 is a plot of the break stress of various neat polymer and blended polymer films versus the concentration of ECOFLEX within the films at a fixed strain rate of 1000 mm/min.;

Figure 7 is a plot of the Water Vapor Permeability Coefficients (WVPC) of various neat polymer and blended polymer films as a function of the concentration of ECOFLEX

1 within the films, and an estimated trend line based on the lowest measured WVPC for a neat  
 2 ECOFLEX film of  $7.79 \times 10^{-3} \text{ g}\cdot\text{cm}/\text{m}^2/\text{d}/\text{mm Hg.};$

3 Figure 8 is a plot of the Water Vapor Permeability Coefficients (WVPC) of various  
 4 neat polymer and blended polymer films as a function of the concentration of ECOFLEX  
 5 within the films, and an estimated trend line based on the highest measured WVPC for a neat  
 6 ECOFLEX film of  $42 \times 10^{-3} \text{ g}\cdot\text{cm}/\text{m}^2/\text{d}/\text{mm Hg.};$  and

7 Figure 9 is a plot of the modulus of various neat polymer and blended polymer films  
 8 versus the concentration of ECOFLEX within the films.  
 9

**DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS**

**I. INTRODUCTION.**

The invention relates to biodegradable polymer blends having greatly improved properties compared to unblended and/or unfilled biodegradable homopolymers and copolymers. Such properties include one or more of improved strength, flexibility, elongation, temperature stability, processability, and dead-fold. Moreover, sheet, films and other articles made from such blends are in many ways superior to conventional plastics, which suffer from their inability to degrade when discarded in the environment, which are not readily printable absent special treatment, and which generally have poor dead-fold properties.

In one aspect of the invention, polymer blends according to the invention may include at least one biopolymer having relatively high stiffness and at least one biopolymer having relatively high flexibility. When blended together, it is possible to derive the beneficial properties from each polymer while offsetting or eliminating the negative properties of each polymer when used separately to make films, sheets and other articles.

The inventive polymer blends may be extruded, blown or otherwise formed into sheets and films for use in a wide variety of packaging materials, such as wraps, bags, pouches, coverings, and laminate coatings. By blending a relatively stiff polymer with a relatively flexible polymer, the inventors have discovered that, in some cases, the beneficial properties of the blend actually exceed the desirable properties of each polymer when used individually. Thus, the surprising result of an unexpected synergistic effect has been demonstrated.

Biopolymers that may be used within blends within the scope of the present invention include, but are not limited to, synthetic polyesters, naturally derived polyesters, polyester amides, polycarbonates, and polyester urethanes, but may also include a variety of natural polymers and their derivatives, such as polymers and derivatives of starch, cellulose,



1 other polysaccharides, and proteins. Particulate fillers, both organic and inorganic, may be  
2 incorporated to improve the dead-fold properties, increase bulk hand feel, reduce cost, and  
3 decrease self-adhesion. Plasticizers may be added to impart desired softening and elongation  
4 properties. Sheets and films may be embossed, crimped, quilted or otherwise textured to  
5 improve bulk hand feel and dead-fold. The biopolymers and biopolymer blends according  
6 to the invention more readily accept and retain print compared to conventional plastics or  
7 waxed papers because they typically include oxygen-containing moieties, such as ester,  
8 amide, or urethane groups, to which inks can readily adhere.

9 The terms "sheets" and "films" are to be understood as having their customary  
10 meanings as used in the thermoplastic and packaging arts. Nevertheless, because the  
11 distinction between what constitutes a "sheet" and what constitutes a "film" largely turns on  
12 the thickness of the article of manufacture, the distinction is somewhat arbitrary (*i.e.* some  
13 articles may constitute both sheets and films). Because the biodegradable compositions  
14 according to the invention can be used to manufacture a wide variety of articles of  
15 manufacture, including articles useful to wrap, package or otherwise package food or other  
16 solid substrates, including sheets and films having a wide variety of thicknesses (both  
17 measured and calculated), it is not the intention of this disclosure to precisely distinguish, in  
18 all cases, between what may arguably constitute a "sheet" versus articles that may arguably  
19 constitute a "film". Therefore, when the present disclosure refers to "sheets and films" and  
20 "sheets or films", the intention is to designate the entire universe of articles of manufacture  
21 that may arguably constitute "sheets", "films" or both.

22 The term "polymer blend" includes two or more unfilled polymers and/or one or  
23 more polymers into which one or more types of solid fillers have been added.  
24

1     **II.     BIODEGRADABLE POLYMERS.**

2             Biopolymers within the scope of the present invention include polymers which  
3     degrade through the action of living organisms, light, air, water and combinations of the  
4     foregoing. Such polymers include a range of synthetic polymers, such as polyesters,  
5     polyester amides, polycarbonates and the like. Naturally-derived semi-synthetic polyesters  
6     (e.g. from fermentation) can also be used. Biodegradation reactions are typically enzyme-  
7     catalyzed and generally occur in the presence of moisture. Natural macromolecules  
8     containing hydrolyzable linkages, such as protein, cellulose and starch, are generally  
9     susceptible to biodegradation by the hydrolytic enzymes of microorganisms. A few man-  
10    made polymers, however, are also biodegradable. The hydrophilic/hydrophobic character  
11    of polymers greatly affects their biodegradability, with more polar polymers being more  
12    readily biodegradable as a general rule. Other important polymer characteristics that affect  
13    biodegradability include crystallinity, chain flexibility and chain length.

14            Besides being able to biodegrade, it is often important for a polymer or polymer  
15    blend to exhibit certain physical properties, such as stiffness, flexibility, water-resistance,  
16    strength, elongation, temperature stability, moisture vapor transmission, gas permeability,  
17    and/or dead-fold. The intended application of a particular polymer blend will often dictate  
18    which properties are necessary in order for a particular polymer blend, or article  
19    manufactured therefrom, to exhibit the desired performance criteria. In the case of sheets and  
20    films suitable for use as packaging materials, desired performance criteria may include  
21    elongation, dead-fold, strength, printability, imperviousness to liquids, breathability,  
22    temperature stability, and the like.

23            Because of the limited number of biodegradable polymers, it is often difficult, or  
24    even impossible, to identify one single polymer or copolymer which meets all, or even most,  
25    of the desired performance criteria for a given application. This is particularly true in the  
26    area of packaging materials. Polymers that have a high glass transition temperature ( $T_g$ ) are

1 often difficult, if not impossible, to blow or cast into films on a mass scale. On the other  
2 hand, polymers that have a very low glass transition temperature typically have relatively low  
3 softening and/or melting points, which makes them difficult to mass produce into sheets and  
4 films without the tendency of blocking, or self adhesion. Moreover, such sheets and films  
5 may lack adequate strength, water vapor barrier properties, high temperature stability, and/or  
6 modulus to be suitable for certain applications, such as in the manufacture of wraps or  
7 laminates coatings.

8 For these and other reasons, biodegradable polymers have found little use in the area  
9 of food packaging materials, particularly in the field of wraps used to package and  
10 encapsulate food items during single serving use. In one aspect of the invention, the  
11 inventors have discovered that sheets and films suitable for making wraps and other  
12 packaging materials can be obtained by blending one or more "stiff", or high glass transition  
13 temperature, polymers with one or more "soft", or low glass transition temperature,  
14 polymers. In another aspect of the invention, polymers or polymer blends can be filled with  
15 particulate fillers, and/or sheets or films made therefrom can be textured, in order to yield  
16 sheets have adequate dead-fold properties.

17  
18 **A. Stiff Polymers.**

19 Even though the use of terms such as "stiff" and "soft" polymers may be somewhat  
20 arbitrary, such classifications are useful when determining which polymers to blend together  
21 in order to obtain a polymer blend having the desired performance criteria, particularly when  
22 the goal is to manufacture a film or sheet suitable for use as a laminate coating, such as on  
23 molded articles made of starch or other moisture sensitive materials, or as a wrap or other  
24 packaging material.

25 In general, those polymers that may be characterized as being relatively "stiff", or  
26 less flexible, typically include polymers which have a glass transition temperature greater

1 than about 10° C. Stiff polymers within the scope of the invention will preferably have a  
 2 glass transition temperature greater than about 15° C., more preferably greater than about 25°  
 3 C., and most preferably greater than about 35° C. The foregoing ranges attempt to take into  
 4 consideration the fact that the "glass transition temperature" is not always a discreet  
 5 temperature but is often a range of temperatures within which the polymer changes from  
 6 being a glassy and more brittle material to being a softer and more flexible material.

7 The glass transition temperature should be distinguished from the melting point of  
 8 a polymer, at or beyond which a thermoplastic polymer becomes plastic and deformable  
 9 without significant rupture. Although there is often a positive correlation between a  
 10 polymer's glass transition temperature ( $T_g$ ) and its melting point ( $T_m$ ), this is not strictly the  
 11 case with all polymers. In some cases the difference between  $T_g$  and  $T_m$  may be large. In  
 12 other cases it may be relatively small. It is generally the case, however, that the melting point  
 13 of a stiffer polymer will typically be greater than the melting point of a softer polymer.

14 Preferred "stiff" polymers within the scope of the present invention include, but are  
 15 not limited to, modified polyethylene terephthalates (such as those manufactured by Du  
 16 Pont), polyesteramides (such as those manufactured by Bayer), polylactic acid-based  
 17 polymers (such as those manufactured by Cargill-Dow Polymers and Dianippon Ink),  
 18 terpolymers based on polylactic acid, polyglycolic acid and polycaprolactone (such as those  
 19 manufactured by Mitsui Chemicals), polyalkylene carbonates (such as polyethylene  
 20 carbonate manufactured by PAC Polymers), and polyhydroxybutyrate (PHB).

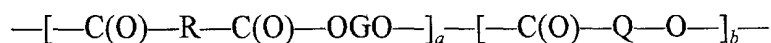
21 A presently preferred stiff biopolymer within the scope of the invention includes a  
 22 range of modified polyethylene terephthalate (PET) polymers manufactured by DuPont, and  
 23 sold under the trade name BIOMAX. Various modified PET polymers of DuPont are  
 24 described in greater detail in U.S. Patent No. 5,053,482 to Tietz, U.S. Patent No. 5,097,004  
 25 to Gallagher et al., U.S. Patent No. 5,097,005 to Tietz, U.S. Patent No. 5,171,308 to  
 26 Gallagher et al., U.S. Patent No. 5,219,646, to Gallagher et al., and U.S. Patent No.

1 5,295,985 to Romesser et al. For purposes of disclosing "stiff" polymers, the foregoing  
2 patents are disclosed herein by reference.

3 In general, the modified PET polymers of DuPont may be characterized as  
4 comprising alternating units of terephthalate and an aliphatic constituent, with the aliphatic  
5 constituent comprising a statistical distribution of two or more different aliphatic units  
6 derived from two or more different diols, such as ethylene glycol, diethylene glycol,  
7 triethylene oxide, polyethylene glycol, lower alkane diols, both branched and unbranched,  
8 and derivatives of the foregoing. A portion of the aliphatic units may also be derived from  
9 an aliphatic diacid, such as adipic acid. In addition, a fraction of the phenylene groups within  
10 the repeating terephthalate units may be sulfonated and neutralized with an alkali metal or  
11 alkaline earth metal base. Both the aliphatic portion of the modified PET polymer as well  
12 as the statistically significant quantity of sulfonated terephthalate units contribute  
13 significantly to the biodegradability of the BIOMAX polymer.

14 Some BIOMAX grades of polymers have a melting point of 200-208° C and a glass  
15 transition temperature of 40-60° C. BIOMAX 6926 is one such grade. It is a relatively  
16 strong and stiff polymer that, when blended with a softer polymer, yields excellent sheets and  
17 films suitable for wrapping and other packaging materials. Films and sheets of BIOMAX  
18 or BIOMAX blends can be cast or blown and then optionally textured in order to impart  
19 desired properties described more fully herein. In addition, or in the alternative, one or more  
20 particulate fillers may be included in order to impart desired properties described more fully  
21 herein.

22 In general, modified polyethylene terephthalates that would be expected to have  
23 properties suitable for use as a "stiff" biodegradable polymer consist essentially of recurring  
24 structural units having the following general formula:



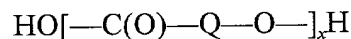
wherein up to about 40 mole % of R is selected from the group consisting of a chemical bond and one or more divalent, non-aromatic, C<sub>1</sub>-C<sub>10</sub> hydrocarbylene radicals, and the remainder of R is at least about 85% mole % p-phenylene radical,

wherein G includes from 0 to about 30 mole % of a polyethylene ether radical selected from the group consisting of:



and the remainder of G is selected from the group consisting of polyalkylene ether radicals of molecular weight at least about 250 (number average), and  $-(CH_2)_2-$ ,  $-(CH_2)_3-$ , and  $-(CH_2)_4-$  radicals,

wherein Q is derived from a hydroxy acid of the formula:



wherein x is an integer and such hydroxy acids have a melting point at least 5° C. below their decomposition temperature, and Q is selected from the group consisting of a chemical bond and hydrocarbylene radicals  $-(CH_2)_n-$ , where n is an integer from 1 to 5,  $-C(R')H-$ , and  $-C(R')HCH_2-$ . wherein R' is selected from the group consisting of  $-CH_3$  and  $-CH_2CH_3$ , and wherein "a" and "b" are mole fractions of the polymer, and the mole fraction "a" may be 0.6 to 1 and, correspondingly, mole fraction "b" may be 0 to 0.4, and wherein about 0.1 to about 15 mole %, preferably about 0.1 to about 2.5 mole %, of the polymer contains alkali metal or alkaline earth metal sulfo groups, especially about 1.5 to about 2 mole % of such groups.

1 Another stiff biopolymer that may be used in manufacturing polymer blends  
2 according to the present invention includes polylactic acid (PLA). Polylactic acid typically  
3 has a glass transition temperature of about 59° C. and a melting point of about 178° C. PLA  
4 has low elongation and is quite hard. It is a strong thermoplastic material that can be  
5 injection molded, extruded, cast, thermoformed, or used as spun or melt-blown fibers to  
6 produce nonwoven goods.

7 Polymers based on or including PLA first found commercial application as medical  
8 sutures in 1970. High polymers of lactic acid ( $M_n=50,000-110,000$ ) are strong  
9 thermoplastics that can be fabricated into useful products that can be broken down by  
10 common soil bacteria. Potential applications of PLA include paper coatings for packaging  
11 (food and beverage cartons), plastic foam for fast foods, microwavable containers, and other  
12 consumer products such as disposable diapers or yard waste bags. PLA can be a  
13 homopolymer or it may be copolymerized with glycolides, lactones or other monomers. One  
14 particularly attractive feature of PLA-based polymers is that they are derived from renewable  
15 agricultural products.

16 Because lactic acid is difficult to polymerize directly to high polymers in a single  
17 step on a commercial scale, most companies employ a two-step process. Lactic acid is first  
18 oligomerized to a linear chain with a molecular weight of less than 3000 by removing water.  
19 The oligomer is then depolymerized to lactide, which is a cyclic dimer consisting of two  
20 condensed lactic acid molecules. This six-member ring is purified and subjected to ring  
21 opening polymerization to produce polylactic acid with a molecular weight of 50,000-  
22 110,000.

23 Because lactic acid has an asymmetric carbon atom, it exists in several isomeric  
24 forms. The lactic acid most commonly sold commercially contains equal parts of L-(+)-  
25 lactic acid and D-(-)-lactic acid and is therefore optically inactive, with no rotatory power.  
26 The racemic mixture is called DL-lactic acid.

Mitsui Chemicals, Inc. manufactures a terpolymer that includes units derived from polylactide, polyglycolide and polycaprolactone that have been condensed together. Thus, this polymer is an aliphatic polymer and may be characterized as a PLA/PGA/PCL terpolymer. Three grade of this polymer are available, H100J, S100 and T100. The H100J grade PLA/PGA/PCL terpolymer has been analyzed to have a glass transition temperatures of 74° C. and a melting point of 173° C.



1 PAC Polymers Inc. manufactures polyethylene carbonate (PEC) having a glass  
2 transition temperature range of 10-28° C. PEC is a "stiff" polymer for purposes of the  
3 present invention

4 Polyhydroxybutyrates (PHBs) can act as either a stiff or soft polymer depending on  
5 their molecular weight, whether they have been modified using chain extenders and/or  
6 branching agents, whether they have been copolymerized with another polymer, and  
7 depending on the other constituents within the overall thermoplastic composition. In this  
8 sense, PHBs are unique among biopolymers and may be of special interest for use in making  
9 wraps, laminate coatings, packaging materials, and the like.

10 As discussed more fully below, native or dried gelatinized starch can be used as  
11 particulate fillers in order to increase the dead-fold properties of sheets and films made from  
12 a particular polymer or polymer blend. However, to the extent that starches become  
13 thermoplastic but retain a substantially portion of their crystallinity, such starches may act  
14 as "stiff", rather than "soft", polymers

15  
16 **B. Soft Polymers.**

17 In general, those biopolymers that may be characterized as being "soft", or less rigid,  
18 typically include polymers which have a glass transition temperature of less than about 0° C.  
19 Soft biopolymers within the scope of the invention will preferably have a glass transition  
20 temperature of less than about -4° C., more preferably less than about -10° C., more  
21 especially preferably less than about -20° C., and most preferably less than about -30° C.  
22 The foregoing ranges attempt to take into consideration the fact that the "glass transition  
23 temperatures" of "soft" polymers are not always discreet temperatures but often comprise a  
24 range of temperatures.

25 Preferred "soft" biopolymers within the scope of the present invention include, but  
26 are not limited to, aliphatic-aromatic copolyesters (such as those manufactured by BASF and

Eastman Chemical), aliphatic polyesters which include repeating units having at least 5 carbon atoms, *e.g.*, polyhydroxyvalerate, polyhydroxybutyrate-hydroxyvalerate copolymer and polycaprolactone (such as those manufactured by Daicel Chemical, Monsanto, Solvay, and Union Carbide), and succinate-based aliphatic polymers, *e.g.*, polybutylene succinate (PBS), polybutylene succinate adipate (PBSA), and polyethylene succinate (PES) (such as those manufactured by Showa High Polymer).

U.S. Patent No. 5,817,721 to Warzelhan et al., and assigned to BASF, discloses a range of aliphatic-aromatic copolyesters within the scope of the invention. Similarly, U.S. Patent Nos. 5,292,783, 5,446,079, 5,559,171, 5,580,911, 5,599,858 and 5,900,322, all to Buchanan et al. and assigned to Eastman Chemical, as well as U.S. Patent Nos. 6,020,393 and 6,922,829 to Khemani, also assigned to Eastman Chemical, all disclose aliphatic-aromatic copolyesters within the scope of the invention. For purposes of disclosing "soft" polymers, the foregoing patents are incorporated herein by reference.

A preferred "soft" polymer that may be used in the manufacture of the inventive polymer blends includes aliphatic-aromatic copolyesters manufactured by BASF and sold under the trade name ECOFLEX. The aliphatic-aromatic copolyesters manufactured by BASF comprise a statistical copolyester derived from 1,4-butanediol, adipic acid, and dimethylterephthalate (DMT). In some cases, a diisocyanate is used as a chain lengthener. Branching agents may also be used to yield branched, rather than linear, copolymers.

Copolymerization of aliphatic monomers, such as diols and diacids, with aromatic monomers, such as diols and diacids (*e.g.*, terephthalic acid or diester derivatives such as DMT), is one way to improve the performance properties of aliphatic polyesters. However, questions have been raised within the industry regarding the complete biodegradability of aliphatic-aromatic copolyesters because aromatic copolyesters such as PET are known to be resistant to microbial attack. Nevertheless, researchers have discovered that aliphatic-aromatic copolyesters are indeed biodegradable and that the biodegradability of these

1 copolyesters is related to the length of the aromatic sequence. Block copolyesters with  
2 relatively long aromatic sequences are less rapidly degraded by microorganisms compared  
3 to random copolyesters having more interrupted aromatic sequences. Film thickness is also  
4 a factor, with thicker films degrading more slowly due to their reduced surface to volume  
5 ratio than thinner films, all things being equal. The polymer presently sold under the name  
6 ECOFLEX S BX 7000 by BASF has a glass transition temperature of -33° C. and a melting  
7 range of 105-115° C.

8 Another "soft" aliphatic-aromatic copolyester is manufactured by Eastman Chemical  
9 Company and is sold under the trade name EASTAR BIO. The aliphatic-aromatic  
10 copolyester manufactured by Eastman is a random copolymer derived from 1,4-butanediol,  
11 adipic acid, and dimethylterephthalate (DMT). One particular grade of EASTAR BIO,  
12 known as EASTAR BIO 14766, has a glass transition temperature of -33° C and a melting  
13 point of 112° C. It has a tensile strength at break in the machine direction of 19 MPa, an  
14 elongation at break of 600%, and a tensile modulus of elasticity of 97 MPa (tangent). It has  
15 an Elmendorf tear strength of 282 g.

16 Polycaprolactone (PCL) is a biodegradable aliphatic polyester having a relatively  
17 low melting point and a very low glass transition temperature. It is so named because it is  
18 formed by polymerizing  $\epsilon$ -caprolactone. The glass transition temperature of PCL is -60° C.  
19 and the melting point is only 60° C. Because of this, PCL and other similar aliphatic  
20 polyesters with low melting points are difficult to process by conventional techniques such  
21 as film blowing and blow molding. Films made from PCL are tacky as extruded and have  
22 low melt strength over 130° C. Also, the slow crystallization of this polymer causes the  
23 properties to change over time. Blending PCL with other polymers improves the  
24 processability of PCL. One common PCL is TONE, manufactured by Union Carbide. Other  
25 manufactures of PCL include Daicel Chemical, Ltd. and Solvay. Though the use of PCL is  
26 certainly within the scope of the invention, it is currently a less preferred soft biopolymer

1 than aliphatic-aromatic polyesters, which give overall better performance for wraps and  
2 laminate coatings.

3        $\epsilon$ -Caprolactone is a seven member ring compound that is characterized by its  
4 reactivity. Cleavage usually takes place at the carbonyl group.  $\epsilon$ -Caprolactone is typically  
5 made from cyclohexanone by a peroxidation process. PCL is a polyester made by  
6 polymerizing  $\epsilon$ -caprolactone. Higher molecular weight PCL may be prepared under the  
7 influence of a wide variety of catalysts, such as aluminum alkyls, organometallic  
8 compositions, such as Group Ia, IIa, IIb, or IIIa metal alkyls, Grignard reagents, Group II  
9 metal dialkyls, calcium or other metal amides or alkyl amides, reaction products of alkaline  
10 earth hexamoniates, alkaline oxides and acetonitrile, aluminum trialkoxides, alkaline earth  
11 aluminum or boron hydrides, alkaline metal or alkaline earth hydrides or alkaline metals  
12 alone. PCL is typically prepared by initiation with an aliphatic diol (HO-R-OH), which  
13 forms a terminal end group.

14       Another "soft" aliphatic polyester that may be used in manufacturing the inventive  
15 polymer blends is polyhydroxybutyrate-hydroxyvalerate copolymer (PHBV), which is  
16 manufactured using a microbial-induced fermentation process. One such PHBV copolyester,  
17 manufactured by the Monsanto Company, has a glass transition temperature of about 0° C.  
18 and a melting point of about 170° C. If possible, PHBV copolyesters should be formulated  
19 and/or modified so as have a glass transition temperature less than about -5° C.

20       In the fermentation process used to manufacture PHBV, a single bacterium species  
21 converts corn and potato feed stocks into a copolymer of polyhydroxybutyrate and  
22 hydroxyvalerate constituents. By manipulating the feed stocks, the proportions of the two  
23 polymer segments can be varied to make different grades of material. All grades are  
24 moisture resistant while still being fully biodegradable. The world producers of PHBV are  
25 Monsanto, with its BIOPOL product, and METABOLIX, with its various grades of

1 polyhydroxy-alkanoates (PHAs). Polyhydroxyvalerate (PHV) is also an example of a "soft"  
2 polymer.

3 As set forth above, polyhydroxybutyrates (PHBs) can act as either a stiff or soft  
4 polymer depending on their molecular weight, whether they have been modified using chain  
5 extenders and/or branching agents, whether they have been copolymerized with another  
6 polymer, and depending on the other constituents within the overall thermoplastic  
7 composition. In this sense, PHBs are unique among biopolymers and may be of special  
8 interest for use in making wraps, laminate coatings, packaging materials, and the like.

9 Another class of "soft" aliphatic polyesters are based on repeating succinate units  
10 such as polybutylene succinate (PBS), polybutylene succinate adipate (PBSA), and  
11 polyethylene succinate (PES). Each of these succinate-based aliphatic polyesters are  
12 manufactured by Showa High Polymer, Ltd. and are sold under the trade name BIONELLE.  
13 PBS (Bionolle 1001) has a glass transition temperature of 30° C. and a melting point of  
14 114° C. PBSA (Bionolle 3001) has a glass transition temperature of -35° C. and a melting  
15 point of 95° C. PES (Bionolle 6000) has a glass transition temperature of -4° C. and a  
16 melting point of 102° C.

17 The target applications for BIONOLLE include films, sheets, filaments, foam-  
18 molded products and foam-expanded products. BIONOLLE is biodegradable in compost,  
19 in moist soil, in water with activated sludge, and in sea water. PBSA degrades rapidly in a  
20 compost environment, so it is similar to cellulose, whereas PBS degrades less rapidly and is  
21 similar to newspaper in terms of biodegradation.

22 BIONOLLE is manufactured according to a patented two-step process of preparing  
23 succinate aliphatic polyesters with high molecular weights and useful physical properties.  
24 In a first step, a low molecular weight hydroxy-terminated aliphatic polyester prepolymer is  
25 made from a glycol and an aliphatic dicarboxylic acid. This polymerization is catalyzed by  
26 a titanium catalyst such as tetraisopropyltitanate, tetraisopropoxy titanium,

1 dibutoxydiacetoacetoxy titanium, or tetrabutyltitanate. In the second step, a high molecular  
2 weight polyester is made by reacting a diisocyanate, such as hexamethylene diisocyanate  
3 (HMDI) with a polyester prepolymer.

4 Showa manufactures PBS by first reacting 1,4-butanediol with succinic acid in a  
5 condensation reaction to form a prepolymer and then reacting the prepolymer with HMDI  
6 as a chain extender.

7 PBSA copolymer is manufactured by first condensing 1,4-butanediol, succinic acid  
8 and adipic acid to form a prepolymer and then reacting the prepolymer with HMDI as a chain  
9 extender.

10 PES homopolymer is prepared by reacting ethylene glycol and succinic acid and  
11 using HMDI or diphenylmethane diisocyanate as a chain extender.

12 Succinate-based aliphatic polyesters are also manufactured by Mitsui Toatsu,  
13 Nippon Shokubai, Cheil Synthetics, Eastman Chemical, and Sunkyon Industries.

14 Finally, although starch, such as modified starch or starch that has been gelatinized  
15 with water and subsequently dried, is known to have a high glass transition temperature (*i.e.*,  
16 70-85° C.) and be very crystalline at room temperature, certain forms of starch in which the  
17 crystallinity has been greatly reduced or destroyed altogether can have very low glass  
18 transition temperatures and may, in fact, constitute "soft" biodegradable polymers within the  
19 scope of the invention. As discussed more fully below, native or dried gelatinized starch can  
20 be used as particulate fillers in order to increase the dead-fold properties of sheets and films  
21 made from a particular polymer or polymer blend. Moreover, to the extent that starches  
22 become thermoplastic but retain a substantially portion of their crystallinity, such starches  
23 may act as "stiff", rather than "soft", polymers. Nevertheless, there exists a range of  
24 thermoplastic starch polymers that can behave as "soft" polymers.

25 For example, U.S. Patent No. 5,362,777 to Tomka is a landmark patent and was the  
26 first attempt to manufacture what is known as thermoplastically processable starch (TPS).

1 TPS is characterized as a thermoplastic starch polymer formed by mixing and heating native  
2 or modified starch in the presence of an appropriate high boiling plasticizer (such as glycerin  
3 and sorbitol) in a manner such that the starch has little or no crystallinity, a low glass  
4 transition temperature, and very low water (less than 5%, preferably less than about 1% by  
5 weight while in a melted state after venting and prior to conditioning). When blended with  
6 appropriate hydrophobic polymers, such as the stiff polymers disclosed herein, *e.g.*,  
7 polyesteramides such as BAK, TPS can have a glass transition temperature as low as -60°  
8 C, and typically below about -20° C.

9 Although it is within the scope of the invention to include thermoplastic polymers  
10 based on starch that include plasticizers such as glycerine, sorbitol, propylene glycol and the  
11 like, it is preferable, when manufacturing wraps for use in covering food products, to utilize  
12 thermoplastic starch polymers that are made without the use of such plasticizers, which can  
13 potentially diffuse into food. Preferred thermoplastic starch polymers for use in making food  
14 wraps may advantageously utilize the natural water content of native starch granules to  
15 initially break down the granular structure and melt the native starch. Thereafter, the melted  
16 starch can be blended with one or more synthetic biopolymers, and the mixture dried by  
17 venting, in order to yield a final polymer blend. Where it is desired to make food wraps or  
18 other sheets or films intended to contact food using a thermoplastic starch polymer made  
19 with a high boiling liquid plasticizer, it will be preferable to limit the quantity of such  
20 thermoplastic starch polymers to less than 10% by weight of the polymer mixture, exclusive  
21 of any solid fillers.

### 22 23 **III. OPTIONAL COMPONENTS.**

24 There are a number of optional components which may be included within the  
25 biodegradable polymer blends of the present invention in order to impart desired properties.

1 These include, but are not limited to, plasticizers, lubricants, fillers, natural polymers and  
2 nonbiodegradable polymers.

3  
4 **A. Plasticizers.**

5 Plasticizers may optionally be added in order to improve processing, such as  
6 extrusion and/or film blowing, or final mechanical properties, particularly of polymer blends  
7 that are relatively stiff. A stiffer polymer blend may be dictated by other performance  
8 criteria, such as high temperature stability, strength, lower elongation, higher dead-fold,  
9 resistance to "blocking" during and after processing, and the like. In such cases, a plasticizer  
10 may be necessary in order to allow the polymer blend to satisfy certain processing and/or  
11 performance criteria.

12 Suitable plasticizers within the scope of the invention, particularly when  
13 incorporated into a polymer blend that is intended to be used in the manufacture of wraps and  
14 other packaging materials that will come into contact with food, will preferably be safe if  
15 consumed, at least in smaller quantities.

16 Optional plasticizers that may be used in accordance with the present invention  
17 include, but are not limited to, soybean oil, castor oil, TWEEN 20, TWEEN 40, TWEEN 60,  
18 TWEEN 80, TWEEN 85, sorbitan monolaurate, sorbitan monooleate, sorbitan  
19 monopalmitate, sorbitan trioleate, sorbitan monostearate, PEG, derivatives of PEG, N,N-  
20 ethylene bis-stearamide, N,N-ethylene bis-oleamide, polymeric plasticizers such as poly(1,6-  
21 hexamethylene adipate), and other compatible low molecular weight polymers.

22 Examples of lubricants include salts of fatty acids, an example of which is  
23 magnesium stearate.  
24



1           **B.    Solid Fillers.**

2           Fillers may optionally be added for a number of reasons, including but not limited  
3 to, increasing the Young's modulus, dead-fold properties, rigidity, and breathability, and for  
4 decreasing the cost and tendency of the polymer blend to "block" or self-adhere during  
5 processing. Certain fillers, like fibers having a high aspect ratio, may increase the strength,  
6 fracture energy and dead-fold properties of the sheets and films according to the invention.  
7 The fillers within the scope of the invention will generally fall within three classes or  
8 categories: (1) inorganic particulate fillers, (2) fibers and (3) organic fillers.

9  
10           **1.    Inorganic Particulate Fillers**

11           The terms "particle" or "particulate filler" should be interpreted broadly to include  
12 filler particles having any of a variety of different shapes and aspect ratios. In general,  
13 "particles" are those solids having an aspect ratio (*i.e.*, the ratio of length to thickness) of less  
14 than about 10:1. Solids having an aspect ratio greater than about 10:1 may be better  
15 understood as "fibers", as that term will be defined and discussed hereinbelow.

16           Virtually any known filler, whether inert or reactive, can be incorporated into the  
17 biodegradable polymer blends. In general, adding an inorganic filler will tend to greatly  
18 reduce the cost of the resulting polymer blend. If a relatively small amount of inorganic filler  
19 is used, the effects on the properties of the final composition are minimized, while adding  
20 a relatively large amount of inorganic filler will increase those effects. In those cases where  
21 adding the inorganic filler will tend to detract from a critical physical parameter, such as  
22 tensile strength or flexibility, only so much of the filler should be added in order to reduce  
23 the cost of the resulting composition, while retaining adequate mechanical properties  
24 required by the intended use. However, in those cases where adding the inorganic filler will  
25 improve one or more desired physical properties of a given application, such as stiffness,  
26 compressive strength, dead-fold, and/or breathability, it may be desirable to increase the

1 quantity of added filler in order to provide this desired property while also proving greatly  
2 decreased cost.

3 It will be appreciated that one of ordinary skill in the art, using a microstructural  
4 engineering approach, can select the types and amount of the various inorganic fillers that  
5 may be included within the polymer blend in order to engineer a final material having the  
6 desired properties while taking advantage of the cost-reducing properties of adding the  
7 inorganic filler.

8 In general, in order to maximize the quantity of inorganic filler while minimizing  
9 the deleterious mechanical effects of adding the filler as much as possible, it may be  
10 advantageous to select filler particles in a manner that decreases the specific surface area of  
11 the particles. The specific surface area is defined as the ratio of the total particle surface area  
12 versus the total particle volume. One way to decrease the specific surface area is to select  
13 particles that have a more uniform surface geometry. The more jagged and irregular the  
14 particle surface geometry, the greater will be the ratio of surface area to volume of that  
15 particle. Another way to decrease the specific surface area is to increase the particle size.  
16 In view of the advantages of decreasing the specific surface area of the inorganic filler, it will  
17 be preferable to include inorganic filler particles having a specific surface area in a range  
18 from about 0.1 m<sup>2</sup>/g to about 400 m<sup>2</sup>/g, more preferably in range from about 0.15 m<sup>2</sup>/g to  
19 about 50 m<sup>2</sup>/g, and most preferably in a range from about 0.2 m<sup>2</sup>/g to about 2 m<sup>2</sup>/g.

20 Related to decreased specific surface area in improving the rheology and final  
21 strength properties of the polymer blends of the present invention is the concept of particle  
22 packing. Particle packing techniques allow for a reduction in "wasted" interstitial space  
23 between particles while maintaining adequate particle lubrication and, hence, mixture  
24 rheology, within the melted polymer blend, while also allowing for more efficient use of the  
25 thermoplastic phase as a binder in the final hardened polymer blends of the present invention.  
26 Simply stated, particle packing is the process of selecting one or more ranges of particle sizes

1 in order that the spaces between a group of larger particles are substantially occupied by a  
2 selected group of smaller particles.

3 In order to optimize the packing density of the inorganic filler particles, differently  
4 sized particles having sizes ranging from as small as about 0.01 micron to as large as about  
5 2 mm may be used. Of course, the thickness and other physical parameters of the desired  
6 article to be manufactured from any given polymer blend may often dictate the upper particle  
7 size limit. In general, the particle packing will be increased whenever any given set of  
8 particles is mixed with another set of particles having an average particle size (*i.e.*, width  
9 and/or length) that is at least about 2 times bigger or smaller than the average particle size  
10 of the first group of particles. The particle packing density for a two-particle system will be  
11 maximized whenever the size ratio of a given set of particles is from about 3-10 times the  
12 size of another set of particles. Similarly, three or more different sets of particles may be  
13 used to further increase the particle packing density.

14 The degree of packing density that will be "optimal" will depend on a number of  
15 factors including, but not limited to, the types and concentrations of the various components  
16 within both the thermoplastic phase and the solid filler phase, the shaping method that will  
17 be employed, and the desired mechanical and other performance properties of the final  
18 articles to be manufactured from a given polymer blend. One of ordinary skill in the art will  
19 be able to determine the optimal level of particle packing that will optimize the packing  
20 density through routine testing. A more detailed discussion of particle packing techniques  
21 can be found in U.S. Patent No. 5,527,387 to Andersen et al. For purposes of disclosing  
22 particle packing techniques that may be useful in maximizing or optimizing particle packing  
23 density, the foregoing patent is incorporated herein by reference.

24 In those cases where it is desired to take advantage of the improved properties of  
25 rheology and binding efficiency utilizing particle packing techniques, it will be preferable  
26 to include inorganic filler particles having a natural particle packing density in a range from

1 about 0.55 to about 0.95, more preferably in range from about 0.6 to about 0.9, and most  
2 preferably in a range from about 0.7 to about 0.85.

3 Examples of useful inorganic fillers that may be included within the biodegradable  
4 polymer blends include such disparate materials as sand, gravel, crushed rock, bauxite,  
5 granite, limestone, sandstone, glass beads, aerogels, xerogels, mica, clay, alumina, silica,  
6 kaolin, microspheres, hollow glass spheres, porous ceramic spheres, gypsum dihydrate,  
7 insoluble salts, calcium carbonate, magnesium carbonate, calcium hydroxide, calcium  
8 aluminate, magnesium carbonate, titanium dioxide, talc, ceramic materials, pozzolanic  
9 materials, salts, zirconium compounds, xonotlite (a crystalline calcium silicate gel),  
10 lightweight expanded clays, perlite, vermiculite, hydrated or unhydrated hydraulic cement  
11 particles, pumice, zeolites, exfoliated rock, ores, minerals, and other geologic materials. A  
12 wide variety of other inorganic fillers may be added to the polymer blends, including  
13 materials such as metals and metal alloys (e.g., stainless steel, iron, and copper), balls or  
14 hollow spherical materials (such as glass, polymers, and metals), filings, pellets, flakes and  
15 powders (such as microsilica).

16 The particle size or range of particle sizes of the inorganic fillers will depend on the  
17 wall thickness of the film, sheet, or other article that is to be manufactured from the polymer  
18 blend. In general, the larger the wall thickness, the larger will be the acceptable particle size.  
19 In most cases, it will be preferable to maximize the particle size within the acceptable range  
20 of particle sizes for a given application in order to reduce the cost and specific surface area  
21 of the inorganic filler. For films that are intended to have a substantial amount of flexibility,  
22 tensile strength, bending endurance and relatively low dead-fold and breathability (e.g.,  
23 plastic bags) the particle size diameter of the inorganic filler will preferably be less than  
24 about 20% of the wall thickness of the film. For example, for a film or sheet having a  
25 thickness of 40 microns, it will be preferable for the inorganic filler particles to have a  
26 particle size diameter of about 8 microns or less.

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1 inorganically filled systems, the inorganic filler will preferably be included in an amount in  
2 a range from about 50% to about 90% by volume.

3 In light of these competing objectives, the actual preferred quantity of inorganic  
4 filler may vary widely. In general terms, however, in order to appreciably decrease the cost  
5 of the resulting polymer blend and/or to impart increased dead-fold, the inorganic filler  
6 component will typically be included in an amount greater than about 10% by weight of the  
7 overall composition, preferably in an amount greater than about 15% by weight, more  
8 preferably in an amount greater than about 20% by weight, more especially preferably greater  
9 than about 30% by weight, and most preferably in an amount greater than about 35% by  
10 weight of the overall composition.

## 11 12 2. Fibers

13 A wide range of fibers can optionally be used in order to improve the physical  
14 properties of the polymer blends. Like the aforementioned fillers, fibers will typically  
15 constitute a solid phase that is separate and distinct from the thermoplastic phase. However,  
16 because of the shape of fibers, *i.e.*, by having an aspect ratio greater than at least about 10:1,  
17 they are better able to impart strength and toughness than particulate fillers. As used in the  
18 specification and the appended claims, the terms "fibers" and "fibrous material" include both  
19 inorganic fibers and organic fibers. Fibers may be added to the moldable mixture to increase  
20 the flexibility, ductility, bendability, cohesion, elongation ability, deflection ability,  
21 toughness, dead-fold, and fracture energy, as well as the flexural and tensile strengths of the  
22 resulting sheets and articles.

23 Fibers that may be incorporated into the polymer blends include naturally occurring  
24 organic fibers, such as cellulosic fibers extracted from wood, plant leaves, and plant stems.  
25 In addition, inorganic fibers made from glass, graphite, silica, ceramic, rock wool, or metal  
26 materials may also be used. Preferred fibers include cotton, wood fibers (both hardwood or

1 softwood fibers, examples of which include southern hardwood and southern pine), flax,  
2 abaca, sisal, ramie, hemp, and bagasse because they readily decompose under normal  
3 conditions. Even recycled paper fibers can be used in many cases and are extremely  
4 inexpensive and plentiful. The fibers may include one or more filaments, fabrics, mesh or  
5 mats, and which may be co-extruded, or otherwise blended with or impregnated into, the  
6 polymer blends of the present invention.

7 The fibers used in making the sheets and other articles of the present invention  
8 preferably have a high length to width ratio (or "aspect ratio") because longer, narrower  
9 fibers can impart more strength to the polymer blend while adding significantly less bulk and  
10 mass to the matrix than thicker fibers. The fibers will have an aspect ratio of at least about  
11 10:1, preferably greater than about 25:1, more preferably greater than about 50:1, and most  
12 preferably greater than about 100:1.

13 The amount of fibers added to the polymer blends will vary depending upon the  
14 desired properties of the final molded article, with tensile strength, toughness, flexibility, and  
15 cost being the principle criteria for determining the amount of fiber to be added in any mix  
16 design. Accordingly, the concentration of fibers within the polymer blends of the present  
17 invention can be included in a broad range from 0% to about 90% by weight of the polymer  
18 blend. If included at all, fibers will preferably be included in an amount in a range from  
19 about 1% to about 80% by weight of the polymer blend, more preferably in a range from  
20 about 3% to about 50% by weight, and most preferably in a range from about 5% to about  
21 30% by weight of the polymer blend.

### 22 23 **3. Organic Fillers**

24 The polymer blends of the present invention may also include a wide range of  
25 organic fillers. Depending on the melting points of the polymer blend and organic filler  
26 being added, the organic filler may remain as a discrete particle and constitute a solid phase

1 separate from the thermoplastic phase, or it may partially or wholly melt and become  
2 partially or wholly associated with the thermoplastic phase.

3 Organic fillers may comprise a wide variety of natural occurring organic fillers such  
4 as, for example, seagel, cork, seeds, gelatins, wood flour, saw dust, milled polymeric  
5 materials, agar-based materials, native starch granules, pregelatinized and dried starch,  
6 expandable particles, and the like. Organic fillers may also include one or more synthetic  
7 polymers of which there is virtually endless variety. Because of the diverse nature of organic  
8 fillers, there will not generally be a preferred concentration range for the optional organic  
9 filler component.

10 Organic fillers can partially or wholly take the place of inorganic fillers. In some  
11 cases, organic fillers can be selected that will impart the same properties as inorganic fillers,  
12 such as to increase dead-fold, the bulk hand feel, breathability and water vapor transmission.  
13 When included at all, the organic filler component will typically be included in an amount  
14 greater than about 5% by weight of the overall composition, preferably in an amount greater  
15 than about 10% by weight, more preferably in an amount greater than about 20% by weight,  
16 and most preferably greater than about 30% by weight of the overall composition.

17  
18 **C. Natural Polymers.**

19 In addition to thermoplastic starch or starch particles, other natural polymers that  
20 may be used within the polymer blends of the present invention comprise or are derivatives  
21 of cellulose, other polysaccharides, polysaccharide gums and proteins.

22 Examples of starches and starch derivatives include, but are not limited to, modified  
23 starches, cationic and anionic starches, and starch esters such as starch acetate, starch  
24 hydroxyethyl ether, alkyl starches, dextrans, amine starches, phosphates starches, and  
25 dialdehyde starches.



Suitable protein-based polymers include, for example, Zein® (a prolamine derived from corn), collagen (extracted from animal connective tissue and bones) and derivatives thereof such as gelatin and glue, casein (the principle protein in cow milk), sunflower protein, egg protein, soybean protein, vegetable gelatins, gluten and mixtures or derivatives thereof.

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1 Examples of common nonbiodegradable polymers suitable for forming sheets and  
2 films include, but are not limited to, polyethylene, polypropylene, polybutylene, PET, PETG,  
3 PETE, polyvinyl chloride, PVDC, polystyrene, polyamides, nylon, polycarbonates,  
4 polysulfides, polysulfones, copolymers including one or more of the foregoing, and the like.  
5

6 **IV. POLYMER BLENDS.**

7 **A. Concentration Ranges of Biopolymers.**

8 The concentrations of the various components within the polymer blend will depend  
9 on a number of factors, including the desired physical and mechanical properties of the final  
10 blend, the performance criteria of articles to be manufactured from a particular blend, the  
11 processing equipment used to manufacture and convert the blend into the desired article of  
12 manufacture, and the particular components within the blend. One of ordinary skill in the  
13 art will be able, in light of the specific examples and other teachings disclosed herein, to  
14 select and optimize the concentrations of the various components through routine testing.

15 In view of the wide variety of polymer blends within the scope of the invention, as  
16 well as the wide variety of different properties that may be engineered within the blends, the  
17 hard and soft polymers may be included within widely varying concentration ranges. The  
18 one or more stiff polymers within the inventive blends will preferably have a concentration  
19 in a range from about 20% to about 99% by weight of the biodegradable polymer blend,  
20 more preferably in a range from about 55% to about 98% by weight, and most preferably in  
21 a range from about 70% to about 95% by weight of the polymer blend.

22 Similarly, the soft polymers will preferably have a concentration in a range from  
23 about 1% to about 80% by weight of the biodegradable polymer blend, more preferably in  
24 a range from about 2% to about 45% by weight, and most preferably in a range from about  
25 5% to about 30% by weight of the polymer blend.

1 The foregoing ranges are measured in terms of the blend of hard and soft polymers  
2 exclusive of any optional components that may be added, as described and identified above.  
3 In the case where only a single biopolymer is used the foregoing ranges to do not apply.  
4

5 **B. Properties of the Polymer Blends.**

6 The polymer blends may be engineered to have any desired property. The properties  
7 of the final article of manufacture will depend on a number of factors, including mix design,  
8 processing conditions, post-formation processing, product size, particularly thickness, and  
9 the like. In the case of sheets or films intended to be used as “wraps”, such as wraps used  
10 to enclose meats, other perishable food items, and especially fast food items (e.g.,  
11 sandwiches, burgers and dessert items), it will generally be desirable to provide sheets and  
12 films having good “dead-fold” properties so that once folded, wrapped or otherwise  
13 manipulated into a desired orientation, such wraps will tend to maintain their orientation so  
14 as to not spontaneously unfold or unwrap, as which occurs with a large number of plastic  
15 sheets and films (e.g., polyethylene).

16 In order to improve the dead-fold properties of sheets or films produced therefrom,  
17 biopolymers may be selected which yield blends having a relatively high Young’s modulus,  
18 preferably greater than about 100 MPa, more preferably greater than about 150 MPa, and  
19 most preferably greater than about 200 MPa. In general, increasing the concentration of the  
20 stiff biopolymer will tend to increase the Young’s modulus. The Young’s modulus may also  
21 be increased by loading the polymer blends with one or more fillers, such as particulate or  
22 fibrous fillers, as described above.

23 In addition to, or instead of, increasing the Young’s modulus to improve dead-fold,  
24 the sheets or films according to the invention may be optionally processed to increase the  
25 “bulk hand feel” of a sheet, which is done by disrupting the generally planar nature of the  
26 sheet or film. This can be done, for example, by embossing, crimping, quilting or otherwise

1 texturing the sheet so as to have regularly spaced-apart or random hills and valleys rather  
2 than simply a smooth, planar sheet. This may be done, for example, by passing the sheet or  
3 film through a pair of knurled or other embossing-type rollers. Such texturing increases the  
4 ability of a sheet to take and maintain a fold, crinkle, creases or other bend, thus improving  
5 the dead-fold properties of the sheet.

6 Another way to increase the surface area of the sheets or films according to the  
7 invention so as to increase their bulk hand feel and/or dead-fold is to include particulate  
8 fillers in which at least a portion of the particles have a particle size diameter that equals or  
9 exceeds the thickness of the polymer film or sheet. In this way, sheets and films can be  
10 manufactured that have dead-fold approaching or equaling 100%, which exceeds the dead-  
11 fold properties of virtually all conventional paper or plastic wraps and sheets currently on the  
12 market. A rare example of a conventional sheet or wrap having 100% dead-fold is aluminum  
13 or other metal foils.

14 The use of fillers coupled with specific processing techniques can be used to create  
15 "cavitation". Cavitation occurs as the thermoplastic polymer fraction is pulled in either a  
16 monoaxial or biaxial direction and the filler particles create a discontinuity in the film or  
17 sheet that increases in size during stretching. During stretching, a portion of the stretched  
18 polymer pulls away from the filler particles, resulting in tiny cavities in the vicinity of the  
19 filler particles. This, in turn, results in greatly increased breathability and vapor transmission  
20 of the sheets and films. It also results in films or sheets having a touch and feel that much  
21 more closely resembles the touch and feel of paper, as contrasted with conventional plastic  
22 sheets and films. The result is a sheet, film or wrap that can be used for applications that are  
23 presently performed or satisfied using paper products (*i.e.*, wraps, tissues, printed materials,  
24 etc.)

25 Articles of manufacture made according to the invention can have any desired  
26 thickness. Thicknesses of sheets and films may range from 0.0001" to 0.1" (about 2.5

1 microns to about 2.5 mm). Sheets and films suitable for wrapping, enclosing or otherwise  
2 covering food items or other solid substrates will typically have a measured thickness  
3 between about 0.0003" and about 0.01" (about 7.5-250 microns), and a calculated thickness  
4 between about 0.00015" and about 0.005" (about 4-125 microns). The measured thickness  
5 will typically be between 10-100% larger than the calculated thickness when the sheets and  
6 films are made from compositions that have a relatively high concentration of particulate  
7 filler particles, which can protrude from the surface of the sheet or film. This phenomenon  
8 is especially pronounced when significant quantities of filler particles having a particle size  
9 diameter that is larger than the thickness of the polymer matrix are used.

10 In view of the foregoing, sheets and films suitable for use as wraps will preferably  
11 have a measured thickness in a range from about 0.0004" to about 0.005" (about 10 to about  
12 125 microns), more preferably in a range from about 0.0005" to about 0.003" (about 12 to  
13 about 75 microns), and most preferably in a range from about 0.001" to about 0.002" (about  
14 25 to about 50 microns). On the other hand, sheets and films suitable for use as wraps will  
15 preferably have a calculated thickness in a range from about 0.0002" to about 0.003" (about  
16 5 to about 75 microns), more preferably in a range from about 0.0003" to about 0.002" (about  
17 7.5 to about 50 microns), and most preferably in a range from about 0.0005" to about 0.0015"  
18 (about 12 to about 40 microns).

19 The difference between the calculated and measured thickness tends to increase with  
20 increasing filler content and also with increasing particle size. Conversely, the difference  
21 between the calculated and measured thickness tends to decrease with decreasing filler  
22 content and also with decreasing particle size. Sheets and films that include no fillers, or  
23 lower quantities of fillers having a particle size diameter that is substantially lower than the  
24 thickness of the polymer matrix, will have a measured thickness that is similar or equal to  
25 the calculated thickness.

### C. Measuring Dead-Fold

The term “dead-fold” refers to the tendency of a sheet or film to maintain a crease, crinkle, fold or other bend. The dead-fold properties of sheets and films can be accurately measured using a standard test known in the art. This test provides the ability to compare and contrast the dead-fold properties of various sheets and films. The following equipment is useful in performing the standard dead-fold test: (1) a semicircular protractor, divided along a 1" diameter semicircle; (2) a weight consisting of a smooth-faced metal block that is  $0.75" \pm 0.05"$  by  $1.25" \pm 0.05"$  and of such a thickness so as to weigh  $50 \text{ g} \pm 0.05 \text{ g}$ ; (3) a 1" x 4" template for cutting test specimens; (4) a timer or stopwatch capable of timing to 1 second; (5) a utility knife or other cutting tool; and (6) a humidity chamber.

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1 The second step is a conditioning step in order to ensure uniformity of test  
2 conditions. The specimens are conditioned by placing them in a humidity chamber at 23°C  
3 and 50% relative humidity for a minimum of 24 hours.

4 The third step is the actual dead-fold test of each conditioned test strip. The  
5 specimen is removed from the humidity chamber and its weight recorded. A light mark is  
6 made 1" from one end of the test strip. The test strip is then placed on a flat surface and bent  
7 over at the mark but without creasing the strip. Next, the weight is placed squarely and  
8 gently over the bend with two thirds (or 0.5") of the weight overlapping the specimen so that  
9 a crease is formed, and with one third or (0.25") of the weight overhanging the crease. The  
10 edges of the weight parallel to the strip should project evenly (about 0.125") beyond each  
11 side of the strip. The weight is allowed to rest on the specimen for 10 seconds. Then it is  
12 removed. After exactly 30 seconds, the angle formed by the crease is measured.

13 The foregoing process is repeated using the other side of the strip and using as many  
14 additional strips as will give a statistically accurate measure of the dead-fold properties of  
15 a given sheet or film. The average angle A is then input into the following formula to  
16 determine the percentage dead-fold C for a given sample:

$$C = 100 * (180 - A) / 180$$

17  
18  
19  
20 If the angle A is 0° (*i.e.*, where the crease is maintained so that no spring back is  
21 observed), the sample has 100% dead-fold ( $C = 100 * (180 - 0) / 180 = 100\%$ ). At the other  
22 extreme, if the angle A is 180° (*i.e.*, where the sample springs all the way back so that the  
23 sample is essentially flat, the sample has 0% dead-fold ( $C = 100 * (180 - 180) / 180 = 0\%$ ). In  
24 the middle, a sample that springs back half way so as to form a right angle has 50% dead-fold  
25 ( $C = 100 * (180 - 90) / 180 = 50\%$ ).

15 It is within the scope of the invention to employ any mixing apparatus known in the  
16 art of manufacturing thermoplastic compositions in order to form the polymer blends of the  
17 invention. Examples of suitable mixing apparatus that can be used to form the blends  
18 according to the invention include a twin-shafted kneader with meshing screws having  
19 kneading blocks sold by the Buss Company, a BRABENDER mixer, a THEYSOHN TSK  
20 045 compounder, which is a twin-shaft extruder with shafts rotating in the same direction  
21 and which has multiple heating and processing zones, a BUSS KO Kneader having a  
22 heatable auger screw, a BAKER-PERKINS MPC/V-30 double and single auger extruder,  
23 single or twin auger OMC extruders, a Model EPV 60/36D extruder, a BATTAGGION  
24 ME100 direct-current slow mixer, a HAAKE Reomex extruder, a COLLIN Blown Film  
25 Extruder, a BATTENFELD-GLOUCESTER Blown Film Extruder, and a BLACK-  
26 CLAWSON Cast Film Extruder.



1 Many of the foregoing mixers are also extruders, which makes them suitable for  
2 extruding films or sheets from the inventive blends according to the invention. Alternatively,  
3 these blends can be made using transfer-line-injection technology where resin manufacturers  
4 can inject the various minor components of these blends into the main poly components  
5 during manufacture. One of ordinary skill in the art will be able to select and optimize an  
6 appropriate manufacturing apparatus according to the desired article to be manufactured.  
7 Once a thermoplastic melt has been formed using any of the above-mentioned mixers, or any  
8 other appropriate mixing and melting apparatus known in the thermoplastic art, virtually any  
9 molding, extrusion or shaping apparatus known in the thermoplastic molding or processing  
10 art can be used to produce finished articles of manufacture.

11 In a preferred embodiment for manufacturing sheets and films, the sheets and films  
12 may be manufactured using a compounding twin screw extruder to prepare the blends, and  
13 a blown film or cast film line to make the films and sheets. Blown films and sheets tend to  
14 have similar, if not identical, strength and other performance properties in the biaxial  
15 direction due to how they are processed (*i.e.*, they are extruded as a tube and then expanded  
16 in all directions by blowing air within the confines of the tube, causing it to expand like a  
17 balloon). Cast films or sheets, on the other hand, unless subjected to biaxial stretching, will  
18 be substantially stronger (*e.g.* will have substantially greater tensile strength) in the machine  
19 direction and will be substantially more tear resistant in the cross-machine direction. When  
20 extruding a thermoplastic material, the polymer molecules tend to be oriented in the machine  
21 direction. Machine direction orientation is further increased if the extruded sheet or film is  
22 passed through a nip to decrease the sheet or film thickness in the machine direction.

23 The sheets and films according to the invention may comprise a single layer or  
24 multiple layers as desired. They may be formed by mono- and co-extrusion, casting and film  
25 blowing techniques known in the art. Because they are thermoplastic, the sheets can be post-  
26 treated by heat sealing to join two ends together to form sacks, pockets, pouches, and the

1 like. They can be laminated onto existing sheets or substrates. They can also be coated  
2 themselves.

3 Monoaxial or biaxial stretching of sheets and films can be used to create cavitation.  
4 Cavitation increase the breathability and vapor transmission of the sheets and films. It also  
5 results in films or sheets having a touch and feel that much more closely resembles the touch  
6 and feel of paper compared to conventional thermoplastic sheets and films.

7  
8 **V. EXAMPLES OF THE PREFERRED EMBODIMENTS.**

9 The following examples are presented in order to more specifically teach  
10 compositions and process conditions for forming the biodegradable blends according to the  
11 present invention, as well as articles therefrom. The examples include various mix designs  
12 of the inventive biodegradable polymer blends as well various processes for manufacturing  
13 the blends and then forming sheets and films therefrom.

14  
15 **EXAMPLES 1-3**

16 Films were manufactured from biodegradable polymer blends having the following  
17 mix designs, with the concentrations being expressed in terms of weight percent of the entire  
18 polymer blend:

19

Example	Biomax 6926	Ecoflex-F	SiO <sub>2</sub>
20 1	94.84%	5%	0.16%
21 2	89.84%	10%	0.16%
22 3	79.84%	20%	0.16%

23  
24

25 The foregoing polymer blends were blended and blown into films at Gemini Plastics,  
26 located in Maywood, California, using DuPont supplied BIOMAX 6926 (both new and old

lots), a silica master batch in BIOMAX 6926 base resin supplied by DuPont, and ECOFLEX-F resin obtained from BASF. The films were blown using a Gemini film blowing extruder (L/D 24/1) equipped with a 2 inch barrier mixing screw containing a Maddock shear mixing tip, and a 4 inch diameter annular die with a die gap of 0.032-0.035".

Even though a typical quantity of silica antiblock was used (*i.e.*, 0.16%), significant blocking of the film was observed for the film made using the mix design of Example 3 (*i.e.* 20% ECOFLEX); however, there was no observed blocking of the 5 and 10% ECOFLEX blends of Examples 1 and 2. For purposes of comparison, films of neat ECOFLEX and BIOMAX were manufactured. The neat ECOFLEX films were manufactured using BASF ECOFLEX-F resin and a 30% talc master batch in the same resin. The neat BIOMAX films (new and old) included 0.16% SiO<sub>2</sub>, while the neat ECOFLEX films included 4.5% talc. The mechanical properties of the BIOMAX/ECOFLEX blend films and the control BIOMAX and neat ECOFLEX-F films were measured under ambient conditions. The data generated is show graphically in Charts 1-8 depicted in Figures 1-8, respectively.

Chart 1, depicted in Figure 1, is a plot of the strain rate versus percent elongation at break for the various films tested. At 500 mm/min. strain rate, both new and old BIOMAX films displayed poor elongation. The neat ECOFLEX films and all of the films made from the BIOMAX-ECOFLEX blends had significantly better elongations than the neat BIOMAX films at all of the strain rates studied. On the other hand, the 20% ECOFLEX blend of Example 3 exhibited equal or better elongation compared to the neat ECOFLEX films at lower strain rates, even though these films included nearly 80% BIOMAX, which was shown to have very poor elongation.

Chart 2, depicted in Figure 2, is a plot of percent elongation versus percentage of ECOFLEX in the BIOMAX/ECOFLEX blends measured at a fixed strain rate of 500 mm/min. As represented by Chart 2, there was a nearly linear improvement in the percent

1 elongation as the concentration of ECOFLEX was increased. Moreover, the 20% ECOFLEX  
2 blend of Example 3 had an elongation as good as the neat ECOFLEX films.

3 Chart 3, depicted in Figure 3, similarly plots the percent elongation versus the  
4 percentage of ECOFLEX in the BIOMAX/ECOFLEX blends measured at a fixed strain rate  
5 of 1000 mm/min. Again, a dramatic improvement in the elongation of the  
6 BIOMAX/ECOFLEX blend was seen as the concentration of ECOFLEX reached 10 and  
7 20%, respectively, although the trend was not as clear as the data in Chart 2, measured at a  
8 fixed strain rate of 500 mm/min.

9 Chart 4, depicted in Figure 4, is a plot of the strain rate versus break stress of the  
10 various films. Again, neat ECOFLEX and all of the BIOMAX/ECOFLEX blends had  
11 significantly better break stress than the neat BIOMAX films at all of the strain rates studied.  
12 Moreover, the BIOMAX/ECOFLEX blends had significantly better break stress than the neat  
13 ECOFLEX films at all strain rates, thus showing that the BIOMAX/ECOFLEX blends are  
14 all stronger in tensile strength than either of neat BIOMAX or ECOFLEX.

15 Chart 5, depicted in Figure 5, is a plot of the break stress versus percent ECOFLEX  
16 in the BIOMAX/ECOFLEX blends of Examples 1-3 measured at a fixed strain rate of 500  
17 mm/min. Once again, a nearly linear increase in break stress was observed as the  
18 concentration of ECOFLEX was increased. Moreover, the 20% blend of Example 3  
19 exhibited the surprising and unexpected result of having nearly twice the break stress as the  
20 neat ECOFLEX film, and nearly three times the break stress as the neat BIOMAX film.

21 Chart 6, depicted in Figure 6, is a plot of the break stress versus percent ECOFLEX  
22 in the BIOMAX/ECOFLEX blends of Examples 1-3 measured at a fixed strain rate of 1000  
23 mm/min. At this strain rate, the 10% ECOFLEX blend of Example 2 had the highest break  
24 stress, with a maximum peak stress of 72 MPa.

25 Charts 7 and 8, depicted in Figures 7 and 8, respectively, plot the water vapor  
26 permeability coefficient (WVPC) of the various films as a function of the concentration of

1 ECOFLEX within the films. In Chart 7, the estimated trend line is based on a WVPC of 7.79  
2  $\times 10^{-3}$  g·cm/m<sup>2</sup>/d/mm Hg, which is the lowest measured WVPC for a neat ECOFLEX film.  
3 In Chart 8, the estimated trend line is alternatively based on a WVPC of  $42 \times 10^{-3}$   
4 g·cm/m<sup>2</sup>/d/mm Hg, which is the highest measured WVPC for a neat ECOFLEX film. The  
5 data in Charts 7 and 8 indicate that the water vapor barrier properties of the 5 and 10%  
6 ECOFLEX blends of Examples 1 and 2 were essentially the same as that of the neat  
7 BIOMAX film. The WVPC data for all samples were measured by the standard procedures  
8 described in the Test Method ASTM F 1249-90.

9 Chart 9, depicted in Figure 9, is a plot of the modulus of various films as a function  
10 of the concentration of ECOFLEX within the films. Surprisingly, the modulus of blends  
11 containing BIOMAX and ECOFLEX are significantly higher than of neat BIOMAX and  
12 ECOFLEX. Because one of the uses of the films manufactured according to the present  
13 invention is as a wrap having good dead-fold properties, and because the degree of dead-fold  
14 is believed to be related to the modulus of a film, blends of BIOMAX and ECOFLEX appear  
15 to have superior dead-fold properties over each of the neat BIOMAX and ECOFLEX films,  
16 with the 5% and 10% blends exhibiting the highest modulus.

#### 17 18 EXAMPLES 4-5

19 Films were manufactured from biodegradable polymer blends having the following  
20 mix designs, with the concentrations being expressed in terms of weight percent of the entire  
21 polymer blends:

22 Example	Biomax 6926	Ecoflex-F	Talc
23 4	79.7%	16.7%	3.6%
24 5	76.7%	16.7%	6.6%

25

1 The films were blown using a Gemini film blowing extruder (L/D 24/1) equipped  
2 with a 2 inch barrier mixing screw containing a Maddock shear mixing tip, and a 4 inch  
3 diameter annular die with a die gap of 0.032-0.035". The film of Example 5 had better dead-  
4 fold properties than the film of Example 4, which might be attributable to the higher  
5 concentration of talc within the blend used in Example 5.

6  
7 EXAMPLE 6

8 A film was manufactured from a biodegradable polymer blend having the following  
9 mix design, with the concentration being expressed in terms of weight percent of the entire  
10 polymer blend:

12 ECOFLEX-F	20%
13 Thermoplastic Starch	50%
14 Polylactic Acid	15%
15 Inorganic Filler	15%

16  
17 The Thermoplastic Starch was obtained from Biotec Biologische Natuerverpackungen  
18 GmbH & Co., KG ("Biotec"), located in Emmerich, Germany. The polylactic acid was  
19 obtained from Cargill-Dow Polymers, LLC, located in Midland, Michigan, USA. The  
20 inorganic filler was calcium carbonate obtained from OMYA, division Pluess-Staufer AG,  
21 located in Oftringen, Switzerland.

22 The foregoing blend was manufactured and blown into sheets using a proprietary  
23 extrusion line thermoplastic starch extrusion/film blowing apparatus manufactured and  
24 assembled specifically for Biotec. In particular, the extrusion/film blowing apparatus was  
25 manufactured by Dr. Collin GmbH, located in Ebersberg, Germany. A detailed description  
26 of an extrusion/film blowing apparatus similar to the one used by Biotec is set forth in U.S.

1 Patent No. 5,525,281 to Lörcks et al. U.S. Patent No. 6,136,097 to Lörcks et al. discloses  
2 processes for manufacturing intermediate thermoplastic starch-containing granulates that can  
3 be further processed to make films and sheets. For purposes of disclosure, the foregoing  
4 patents are incorporated herein by reference.

5 The film had a modulus of 215.65 MPa. Thus, it had excellent dead-fold properties  
6 as a result of the inclusion of the inorganic filler and the polylactic acid, which is a generally  
7 stiff, crystalline polymer at room temperature. As set forth above, PLA has a glass transition  
8 temperature between 50-60° C. The ECOFLEX and thermoplastic starch (TPS) both acted  
9 as soft, low glass transition temperature polymers. The TPS, when blended with additional  
10 polymers and at very low water, has a glass transition temperature approaching -60° C. The  
11 ECOFLEX and TPS thus assisted the blowability and flexibility of the blend. The TPS also  
12 increased the natural polymer content, thus making the film more biodegradable.

#### 13 14 EXAMPLE 7

15 A film was manufactured from a biodegradable polymer blend having the following  
16 mix design, with the concentration being expressed in terms of weight percent of the entire  
17 polymer blend:

18		
19	Thermoplastic Starch	30%
20	BAK 1095	60%
21	Inorganic Filler	10%
22		

23 The thermoplastic starch was obtained from Biotec. The BAK 1095 was obtained  
24 from Bayer AG, located in Köln, Germany, and was an aliphatic-aromatic polyesteramide.  
25 The inorganic filler was calcium carbonate obtained from OMYA, division Pluess-Stauffer  
26 AG, located in Oftringen, Switzerland.

The foregoing blend was manufactured and blown into sheets using the proprietary thermoplastic starch extrusion/film blowing apparatus described in Example 6. The film had excellent dead-fold properties as a result of the inclusion of the inorganic filler and the BAK 1095, which is a somewhat stiff, crystalline polymer at room temperature even though it is classified as "film grade". As set forth above, BAK 1095 behaves as if it has a glass transition temperature of at least 10° C. Because the glass transition temperature of BAK 1095 is relatively low compared to PLA, considerably more BAK could be included without destroying the film-blowing properties and flexibility of the resulting film. The TPS acted as the soft, low glass transition temperature polymer, and further assisted the blowability and flexibility of the blend. It also increased the natural polymer content, thus making the film more biodegradable.

#### EXAMPLES 8-12

Films were manufactured from biodegradable polymer blends having the following mix designs, with the concentrations being expressed in term of weight percent of the entire polymer blend:

Example	Biomax 6926	Ecoflex F	Talc	TiO <sub>2</sub>	CaCO <sub>3</sub>
8	76%	15%	4.5%	4.5%	--
9	85.5%	9.5%	--	5%	--
10	70%	17.5%	--	2.5%	10%
11	66%	16.5%	--	2.5%	15%
12	58%	24%	--	3%	15%

The talc was supplied by Luzenac, located in Englewood, Colorado, having a particle size of 3.8 microns. The titanium dioxide was supplied by Kerr-McGee Chemical,



LLC, located in Oklahoma City, Oklahoma, grade TRONOX 470, having a particle size of 0.17 micron. The calcium carbonate was supplied by Omnia, located in Lucerne Valley, California, particle size of 2 microns. The foregoing blends were manufactured on a Werner Pfeiderer ZSK twin-screw extruder, and blown into sheets using a Gemini film blowing extruder (L/D 24/1) equipped with a 2 inch barrier mixing screw containing a Maddock shear mixing tip, and a 4 inch diameter die. All of the films had excellent dead-fold properties. The polymer blends of Examples 10-12 were also extruded into sheets using a single screw extruder and a 14 inch flat cast-film die, and the usual nip-rolls and film take-up assembly normal to such a system. All of these films also had excellent dead-fold properties.

#### Examples 13-61

Blown and cast films and sheets were manufactured from biodegradable polymer blends having the following mix designs, with the concentrations being expressed in term of weight percent of the entire polymer blend:

Example	PLA	Biomax	Ecoflex BX 7000	Eastar Bio Ultra	Eastar Bio GP	CaCO <sub>3</sub>	TiO <sub>2</sub>	Starch
13	30%	0%	45%	0%	8.25%	14.5%	2.25%	0%
14	30%	0%	30%	0%	13.2%	23.2%	3.6%	0%
15	30%	0%	25%	0%	11.55%	20.3%	3.15%	10%
16	50%	0%	25%	0%	8.25%	14.5%	2.25%	0%
17	50%	0%	10%	0%	13.2%	23.2%	3.6%	0%
18	50%	0%	5%	0%	11.55%	20.3%	3.15%	10%
19	50%	0%	0%	0%	16.5%	29.0%	4.5%	0%
20	50%	0%	0%	0%	13.2%	23.2%	3.6%	10%
21	50%	0%	0%	0%	11.55%	20.3%	3.2%	15%
22	50%	0%	0%	0%	9.9%	17.4%	2.7%	20%
23	50%	0%	0%	0%	8.25%	14.5%	2.25%	25%

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24	27%	0%	64%	0%	2.97%	5.22%	0.81%	0%
25	25%	0%	58%	0%	5.61%	9.86%	1.53%	0%
26	23%	0%	54%	0%	7.59%	13.34%	2.07%	0%
27	30%	0%	40%	0%	0%	0.0%	0.0%	30%
28	15%	0%	60%	0%	0%	0.0%	0.0%	25%
29	25%	0%	25%	0%	16.5%	29.0%	4.5%	0%
30	20%	0%	20%	0%	19.8%	34.8%	5.4%	0%
31	35%	0%	5%	0%	19.8%	34.8%	5.4%	0%
32	40%	0%	10%	0%	16.5%	29.0%	4.5%	0%
33	50%	0%	0%	0%	16.5%	29.0%	4.5%	0%
34	20%	0%	0%	20%	19.8%	34.8%	5.4%	0%
35	27%	0%	36%	0%	3.3%	5.8%	0.9%	27%
36	21%	0%	28%	0%	9.9%	17.4%	2.7%	21%
37	28.5%	0%	38%	5%	0%	0%	0%	28.5%
38	40%	0%	0%	7%	16.5%	29.0%	4.5%	3%
39	40%	0%	7%	0%	16.5%	29.0%	4.5%	3%
40	50%	0%	0%	0%	16.5%	29.0%	4.5%	0%
41	20%	0%	0%	20%	19.8%	34.8%	5.4%	0%
42	30%	0%	0%	14%	16.5%	29.0%	4.5%	6%
43	40%	0%	0%	14%	13.2%	23.2%	3.6%	6%
44	0%	40%	0%	14%	13.2%	23.2%	3.6%	6%
45	0%	50%	0%	0%	16.5%	29.0%	4.5%	0%
46	0%	45%	0%	0%	18.15%	31.9%	4.95%	0%
47	0%	40%	0%	0%	19.8%	34.8%	5.4%	0%
48	0%	40%	0%	0%	19.8%	34.8%	5.4%	0%
49	40%	0%	14%	0%	13.2%	23.2%	3.6%	6%
50	0%	30%	0%	7%	19.8%	34.8%	5.4%	3%
51	0%	35%	0%	7%	18.15%	31.9%	4.95%	3%
52	0%	38%	0%	1.4%	19.8%	34.8%	5.4%	0.6%

53	0%	35%	0%	3.5%	19.8%	34.8%	5.4%	1.5%
54	40%	0%	0%	14%	13.2%	23.2%	3.6%	6%
55	40%	0%	0%	0%	26.7%	22.7%	3.5%	7.1%
56	40%	0%	0%	13.8%	12.9%	22.7%	3.5%	7.1%
57	40%	0%	0%	26.7%	0%	22.7%	3.5%	7.1%
58	40%	0%	0%	13.8%	12.9%	22.7%	3.5%	7.1%
59	40%	0%	0%	0%	26.7%	22.7%	3.5%	7.1%
60	40%	0%	0%	14%	13.2%	23.2%	3.6%	6%
61	0%	50%	0%	0%	16.5%	29.0%	4.5%	0%

The compositions of Examples 13-59 were all processed and blown into films using a COLLIN Blown Film Extruder. The films made using the compositions of Examples 30-34, 36, 38, 41 and 43 were tested and found to have dead-folds of 100%, 92%, 92%, 91%, 100%, 100%, 100%, 100% and 100%, respectively. Although films made from the other compositions were not tested for dead-fold, they would be expected to have relatively high dead-fold compared to conventional biopolymers (*i.e.*, at least about 80%). The water vapor transmission rate for films made using the compositions of Examples 36, 38, 41 and 43 were 91.94, 91.32, 98.29 and 80.31 g/m<sup>2</sup>/day, respectively.

The composition of Example 60 was processed and blown into a film using a BATTENFELD-GLOUCESTER Blown Film Extruder. A film made from this composition was found to have a water vapor transmission rate of 42.48 g/m<sup>2</sup>/day.

The composition of Example 61 was processed and blown into various films using both a BATTENFELD-GLOUCESTER Blown Film Extruder and a BLACK-CLAWSON Cast Film Extruder. The film formed using the BATTENFELD-GLOUCESTER Blown Film Extruder apparatus was tested and found to have a dead-fold of 100%. Two different thicknesses of films were formed using the BLACK-CLAWSON Cast Film Extruder, one having a thickness of 1.3 mils (0.0013") and another having a thickness of 1.8 mils

(0.0018"). Both had a distinctive machine direction orientation because they were cast, rather than blown, films. The 1.3 mil film had a dead-fold of 99%, and the 1.8 mil film had a dead-fold of 100%.

The present invention may be embodied in other specific forms without departing from its spirit or essential characteristics. The described embodiments are to be considered in all respects only as illustrative and not restrictive. The scope of the invention is, therefore, indicated by the appended claims rather than by the foregoing description. All changes which come within the meaning and range of equivalency of the claims are to be embraced within their scope.

What is claimed and desired to be secured by United States Letters Patent is: